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CHARACTERIZATION OF DIOXINS, FURANS AND PCBs IN SOIL SAMPLES COLLECTED FROM THE DENVER FRONT RANGE AREA

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APPROVALS

This report has been prepared for and by the U.S. Environmental Protection Agency, Region 8. The results and conclusions presented in this report are accepted by EPA Region 8 as correct and appropriate.

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1.0 INTRODUCTION

Overview of the Issue

Dioxins are a class of chemicals that are of potential human health concern because they may pose an increased risk of cancer and other adverse health effects at very low exposure levels. As a consequence, regulatory agencies often need to evaluate potential risks from dioxins at sites of regulatory concern, especially sites involved in the manufacture of certain chlorinated pesticides and other chemicals.

However, the occurrence of dioxins in site soils is not always evidence of a site-specific release, since dioxins can be formed and released to the environment from multiple sources. Historically, the largest source has been atmospheric deposition resulting from incineration of medical and municipal organic wastes which have high contents of chlorine (EPA 1994a). In addition, dioxins can be formed from the combustion of many other types of organic precursors such as coal and wood, so dioxins can also be released from power plants, wood burning furnaces, forest fires, etc. (EPA 1998b).

Because of these multiple potential sources of dioxin release to the environment, it is often difficult to know whether dioxin levels observed in soil at a particular location are attributable to some specific local "point" source (e.g., chemical manufacturing, releases from an on-site incinerator, etc.), or whether the levels represent typical "ambient" or ubiquitous concentrations due to other area or non-point sources. Therefore, information on typical ranges of dioxin levels in ambient soils is needed to scientifically evaluate whether particular sites of regulatory concern are contaminated with dioxins attributable to some site-specific source and release pathway.

As discussed in greater detail below, some studies have measured typical ambient levels of dioxins in soil, but the data from these studies are very limited and are of uncertain quality and relevance. Consequently, the current study was planned and performed in order to obtain data that are suitable for supporting comparisons of dioxin levels at a site of concern with levels observed in the general environment.

Definition of Dioxins

2,3,7,8-Tetrachlorodibenzodioxin (TCDD) is the most potent of a group of related chemicals that include other congeners of dioxins, furans, and polychlorinated biphenyls (PCBs). For the purposes of this report, the term "dioxins" is meant to refer to the set of 17 dioxins and furans and the set of 12 PCBs that bind to the aryl hydrocarbon (Ah) receptor and possess toxic characteristics similar to those of TCDD. These so-called "Ah-agonists" are listed in **Table 1**.

Not all dioxin congeners are equally toxic. The relative toxicity of a congener, compared to that of TCDD, is expressed in terms of the Toxicity Equivalency Factor (TEF). Table 1 lists consensus TEF values for mammals (including humans), birds, and fish. These TEF values were developed by a panel of experts assembled by the World Health Organization (Van den Berg et al. 1998). Note that TEFs are often based on limited data, and so they are only approximations of the relative toxicity of each congener, rounded to the nearest half order of magnitude.

Calculation of TCDD-Equivalents in Soil

The aggregate toxicity of a mixture of different dioxins in an exposure medium (soil, food web items, etc.) is a complex function of a) concentrations of each congener in media, b) daily intake of the medium, c) absorption of each congener from that medium, and d) congener-specific TEF values. However, for purposes of screening-level evaluations of dioxin concentrations in soil samples, it is usually most convenient to calculate the concentration of TCDD-Equivalents (TEQ) present in the soil, as follows:

$$TEQ = \mathop{\mathrm{Sum}}_{i=1}^{i=29} (C_i \cdot TEF_i)$$

This approach allows a comparison of different soils in terms of a single value that is proportional to toxicity (the TEQ for the sample), rather than having to compare up to 29 different concentration values. For the purposes of this report, the TEQ values are based on the TEFs for mammals (humans).

Review of Existing Data on Ambient TEQ Levels

Data on typical dioxin levels in ambient soil are limited. In the United States, a summary of TEQ levels (only from measuring some or all of the 17 dioxin and furan congeners, but not dioxin-like PCBs) at 95 sample locations yielded an estimated mean of 8.0 ppt and a standard deviation of 5.7 ppt (USEPA 1994a). Assuming that the distribution of dioxin (TEQ) values in soil is likely to be represented by a lognormal distribution, then these data suggest that most (approximately 90%) values are likely to lie in the range of 2 - 20 ppt. Reports from other sites such as Times Beach, Mo (that focused mostly on TCDD), of incinerator plumes in Ohio, and of recent studies on soils in states that included Mississippi, Minnesota, and Washington, plus local EPA Region 8 hazardous waste sites, all indicated that background surface soils appear to have TEQ levels for dioxins and furans in the low ppt range, spanning perhaps two orders of magnitude. These results are summarized in **Figure 1**.

In considering these data, it is important to recognize that a number of factors may limit the accuracy and relevance of the data, including the following:

1. Much information is from older studies performed 5 to 20 years ago. Because dioxin emission rates have been decreasing over time, older data are inherently less relevant and less applicable

than current data.

2. In the past (and even in some current studies), Method Quantitation Limits (MQLs) were often higher than background levels in soil, which prevents reliable quantitation of true background levels. In some cases, MQLs were not even reported or defined.
3. In some studies, only partial sets of the 17 dioxin/furan Ah-agonist congeners were measured. In these cases, the true TEQ (the sum of the 29 Ah-agonists listed in Table 1) is likely to be underestimated.
4. The TEFs that are currently recommended to calculate the TEQ level in soil (see Table 1) differ from those used in the past, so older studies in which only the TEQ was reported are difficult to directly compare and interpret.
5. Most previous studies did not stratify measured values according to land-use. Thus, if there are significant differences between land-use categories, such non-stratified studies are difficult to use for background assessments.
6. Variations occurred in the depth of soil samples collected. Because dioxin levels are likely to be higher in surface soil than subsurface soil, studies conducted using different soil depths are difficult to accurately compare.
7. Most soil collections were apparently measured in "bulk" (non-sieved, larger particulate) soil samples. However, both humans and animals are believed to be exposed mainly to the fine fraction (less than 250 Fm maximum diameter) of soil particles. If dioxin levels are higher in the fine fraction, older "bulk" data may underestimate actual exposure levels.
8. Quality control data were not reported in all studies, making it difficult to judge the accuracy and precision of the data.

Purpose of This Study

Because of the multiple potential sources of dioxin release to the environment, and because of the limitations in the existing database on dioxin levels in ambient soils, this project was planned and performed to **characterize existing dioxin concentrations in surface soils from multiple locations and multiple land use categories in the Denver front range area.**

The data collected during this study will be used by EPA risk assessors and risk managers to help determine whether the concentration of dioxins in surface soils at CERCLA sites, RCRA sites, and other sites of potential regulatory concern, are higher than those which occur in similar lands that are not known to be impacted by any specific point sources of dioxin releases. If the soil concentration for dioxin at one or more sites is higher than the appropriate reference level, then risk assessors and risk managers will need to evaluate if dioxin should be considered to be a chemical of potential concern to either humans or ecological receptors, and to make informed decisions about how to protect people and the environment at these sites.

2.0 METHODS

A detailed description of the rationale, methods, and Standard Operating Procedures (SOPs) used in this study are provided in the Project Plan for the study (USEPA 1999c). A summary of key elements of the study design and of the methods employed is presented below.

2.1 Soil Sampling

Study Area

The area selected for investigation in this project encompasses the Denver front range area, as defined by a square that is approximately 30 miles on a side, centered approximately on Denver, Colorado. This area encompasses approximately 1,000 square miles, and includes a wide variety of different land uses.

Property Ownership

All soil sampling locations in this study were on governmental (public) lands, including properties controlled by Federal, State, or County agencies.

Spatial and Land-Use Representativeness

In order to be generally useful, the data set of ambient soil concentration values in Denver area soils must be representative of the range of conditions which exist within the study area. That is, samples from only one area might not be representative either of the typical level or of the range of variability observed over the full study area. Likewise, samples collected from only one type of land use might not be representative, since some land uses might tend to have higher or lower levels of dioxins than others. For the purpose of this study, five different types of land use categories were considered, as defined below:

Residential - Land that is within 200 feet and adjacent to residential development, but which is not within private yards. This may include public parks, neighborhood greenbelts and trails, and street medians. Schools and playgrounds are not included in this category.

Agricultural - Land that is now, or has been within the past 40-50 years, tilled and used for crop production.

Open space - Land that is greater than 20 acres in area that has not been developed or improved and that is essentially in its natural state with the exception of minor changes, such as hiking trails or dirt access roads; this category may include some lands used for grazing of livestock.

Commercial - Land that is developed and used for commercial purposes, such as shopping centers, restaurants, office buildings, post offices, etc.

Industrial - Land that is used for manufacturing, refining, warehousing, or transportation purposes (e.g., garages, railroads, etc.).

As discussed in the Project Plan (USEPA 1999c), the goal was to collect approximately 30 samples from each of these five different land uses, for a total of 150 samples. The actual number of samples collected was as follows:

Land Use	Target	Actual
Agricultural	30	27
Commercial	30	30
Industrial	30	31
Open Space	30	37
Residential	30	40
Total	150	165

Figure 2 is a map which shows the sampling locations and the land use at each location. As seen, the samples are well-distributed across the study area, helping to ensure that the data are fully representative.

Sampling Depth

Because dioxins nearly always bind tightly to soil, it is expected that any dioxin contamination in soil that has occurred chiefly as result of atmospheric deposition and/or application of herbicides will be restricted to the surface. Thus, surface soil is the exposure medium of chief concern for both human and ecological receptors. Therefore, all soil samples collected for this study were grab samples collected at 0-2 inches in depth.

Soil Types

Soil samples were collected at each designated sampling station without regard to the soil type at that station. However, because dioxin levels could tend to vary as a function of soil type, field observations on the nature of the sample (color, texture, etc.) were recorded, and the total organic carbon level of the sample was measured.

Temporal Bounds

Soil samples were not collected from locations that were known to have been covered with fill or used for borrow material within the last 10 years, since the dioxin content of such recently disturbed areas might not be representative of surrounding undisturbed background areas.

Sample Collection and Storage

Samples were collected using a stainless steel trowel. A ruler was used to ensure that the actual depth to which soil was collected was within ½ inch of the target (i.e., a bottom depth of no less than 1.5 inches and no greater than 2.5 inches). The soil was placed directly into a clean 16-oz amber glass jar with a teflon-lined lid, and these bottles were stored at room temperature in the dark.

2.2 Sample Preparation

All samples collected in the field were submitted under chain-of-custody to Columbia Analytical Services (CAS) for sample preparation. Each sample was air dried to constant weight, followed by coarse-sieving through a #10 (2 mm) stainless steel screen. The fraction passing the screen is referred to as the "bulk" fraction. Approximately 100 g of the bulk sample was placed in a clean amber glass jar and stored for future used. The remainder of the bulk sample was further sieved through a 60-mesh (250 um) sieve in order to isolate soil particles less than 250 um in diameter. This fraction (referred to as the "fine" fraction) was isolated because it is believed that fine soil particles are more likely to be ingested by hand to mouth contact that coarse particles, and hence it is concluded that this soil fraction is the most relevant for evaluating human health risk. All of the fine material passing the 250 um sieve was placed in a clean amber glass bottle for analysis and storage.

2.3 Sample Analysis

Following sample preparation as described above, samples were submitted under chain of custody to Midwest Research Institute (MRI) for chemical analysis. Analysis of dioxins in soil samples requires a sophisticated extraction and clean-up procedure. This procedure is detailed in USEPA (1999c) Standard Operating Procedure 11. In brief, the congeners are determined using isotope dilution method via high resolution gas chromatography/mass spectrometry (HRGC/HRMS). Samples are fortified with ^{13}C-labeled PCDD/PCDF/PCB isomers and extracted with an organic solvent. Before cleanup of the extract, the analytes are exchanged into hexane and fortified with ^{37}Cl-labeled *2,3,7,8*-tetrachlorodibenzo-*p*-dioxin. Finally, the extract is sequentially partitioned against concentrated acid and base solutions.

The Method Detection Limit (MDL) for dioxins/furans by this analytical method is defined as a signal that is 2.5 times the average signal noise. An estimate of the average signal noise is available for each analyte in each samples, so the MDL varies from sample to sample and from analyte to analyte. The Method Quantitation Limit (MQL) is based on the lowest calibration standard used and is defined as a signal that is 10-times the average signal noise. Because the noise level varies from sample to sample and analyte to analyte, DLs and QLs also vary from sample to sample and from congener to congener. All congeners that yielded signals that were below the sample-specific detection limit for that congener (signal/noise ratio < 2.5) were evaluated by assuming a concentration value equal to ½ the detection limit for that congener.

2.4 Quality Assurance

A number of steps were taken to obtain data that would allow an assessment of the accuracy and reliability of the data collected. Key elements of the Quality Assurance program are summarized below.

Performance Evaluation Samples

Performance Evaluation (PE) samples are samples of soil that contain know quantities of analyte and that are submitted blind to the analytical laboratory. In this study, three different PE samples were used. These were obtained from EPA's Quality Assurance Technical Support (QATS) laboratory . Nominal values (ppt as TEQ in bulk soil, based on PCDD/PCDF congeners only) are listed below:

Description	**Nominal Value (ppt TEQ in bulk soil)**
Native western soil	< 2
Low standard	35
Medium standard	59

One aliquot of each these three QATS PE samples was submitted to the laboratory along with each set of 14 field samples. In some cases the sample was submitted un-sieved (bulk), and in other cases the samples was sieved, and only the fine fraction was analyzed.

Field Splits and Duplicates

A field duplicate is a second sample of soil collected at the same location as the first sample was collected, by alternating scoops of soil that was placed into the sample jar and into the duplicate jar. A sample split is a specimen that is generated by dividing a single field sample into two parts; in this case, a second aliquot from four total aliquots of sieved soil was submitted from the EPA archiving laboratory in Golden, CO, to the analytical laboratory. Both field duplicate and laboratory split samples were given unique and random identifying labels, so as to be blind to the laboratory analysts. Analysis of these types of samples provided data on the variability within and between related samples. One sample of each type was submitted to the laboratory with each set of about 14 field samples.

Laboratory Quality Control Samples

Laboratory QA samples are samples prepared and run by the laboratory in a non-blind fashion to monitor the performance of the analytical method. Laboratory QA samples included **Method Blanks** (analyte-free soil), **Laboratory Control Samples** (similar to PE samples, but the identity and true concentration are known to the laboratory), and **Method Duplicates** (investigative samples that are split prior to sample preparation at the analytical laboratory).

Data Validation/Verification

All data from MRI were subjected to a data verification check that was performed by Rocky Mountain Arsenal (RMA) contractors (see SOP 12 in the Project Plan). No significant problems were detected in this verification check.

Following verification, all data values were reviewed by EPA to assign data usability flags. **Table 2** summarizes the data quality flags codes that were used, along with a description of the effect of the flag on the data usability assessment. In accord with USEPA (1992) data usability guidelines (Data Usability for Risk Assessment in Superfund), these flags are used for producing two data sets:

1) a semi-quantitative set of results with a value (actual or proxy as per above flags) for each congener; this result is referred to in this report as the "**Full**" TEQ value

2) a quantitative data set with more certain quantitative values (actual or proxy as per above flags) for only the congeners that have no disqualifying flags (D, JN, R and LT); this result is referred to in this report as the "**Quantitative**" TEQ value.

This distinction is made to help evaluate the effects of estimated values on TEQs and to evaluate profiles.

3.0 RESULTS

Detailed analytical results for each field sample are presented in **Appendix A1**, and detailed results for each QA sample run as part of this study are presented in **Appendix A2**. Graphical representations are presented in **Appendix B**. The results are summarized below.

3.1 TEQ Values

Of the 165 field samples collected during this study, sufficient sample mass was available to sieve and analyze the fine fraction for 162 samples. The full TEQ results for these 162 samples are shown in

Table 3 (Panel A). The values for the three other samples (bulk analysis only) are shown in the footnote to Panel A. Maps showing the spatial pattern of all 165 results (fine and bulk) are presented in **Appendix C**.

As seen, there is a fairly wide range of full TEQ values observed in Denver area soils (fine fraction), from a minimum of less than 0.1 ppt TEQ up to a maximum of 155 ppt TEQ. The distributions of values tends to be right skewed, and all but the residential data set may be reasonably approximated by lognormal probability density functions:

Data Set (ln-transformed)	K-S Distance	P	Lognormal Approximation ?
Agricultural	0.125	0.329	Yes
Commercial	0.084	0.778	Yes
Industrial	0.069	0.868	Yes
Open Space	0.124	0.172	Yes
Residential	0.167	0.013	No

Visual inspection of the raw data (Appendix A) suggest that two data points (the maximum value for the commercial and the residential data sets) might be outliers. This was confirmed by a simple outlier test (based on the mean plus 2.5 standard deviation of the log-transformed values), which indicated that these two data points were very unlikely to drawn from the same distribution as the reminder of the points in each group. The basis for these two outliers is not known, but might be due to the presence of some specific (but unknown) point source at these two sampling locations. Based on the conclusion that these two samples are not representative of their respective land uses, they were excluded from further analysis. The lower panel of Table 3 shows the summary statistics after exclusion of these two points.

Figure 3 is a graphical representation of the distributions (after the outliers have been excluded). As seen, while all of the values are relatively low, samples collected on lands that were ranked as agricultural or open space tended to have values somewhat lower than those from commercial or industrial areas. The distribution for residential samples is generally similar to that for commercial properties. In interpreting this finding, it is important to remember that none of the “residential” sampling locations are actually on private residential properties, but rather all are on governmental properties located in or near residential neighborhoods. In some cases, the current land use is more similar to light commercial/industrial than residential (e.g., pump stations, park-and-ride stations). In addition, because a full land use history is not available for most of these properties, it is possible that some of these governmental properties may have been used in the past for activities that tended to increase dioxin levels slightly.

3.2 Contribution of PCBs

The TEQ values presented in Table 3 are based on the sum of TEQ values across 17 dioxin/furan congeners. As noted above, some PCBs also posses dioxin-like activity and may contribute to the levels of TEQ in soil. Summary statistics (averaged across land use) are presented below:

Land Use	Full TEQ (ppt)			% PCBs
	D/F	PCB	Total	
Agricultural	1.6	0.3	1.9	18%
Commercial	6.6	2.2	8.8	25%
Industrial	10.7	5.4	16.1	33%
Open Space	1.7	1.2	3.0	42%
Residential	7.1	1.6	8.7	19%
Total	5.5	2.1	7.7	28%

As seen, PCBs contribute about 1 ppt or less to the full TEQ in agricultural and open space soils, but may contribute about 2-5 ppt in commercial, industrial or residential samples. On average across all samples, PCBs contribute about 28% of the total TEQ (summed across all 29 D/F and PCB congeners).

3.3 Comparison of Bulk to Fine

As noted above, most of the samples analyzed in this study were sieved to isolate the fine fraction (< 250 um), because it is suspected that humans are likely to be exposed mainly to particles in this size range. In most cases, the ratio of full TEQ in fine samples compared to the matched bulk samples was about 1.3 to 1 (range = 0.8 to 2.3), indicating that there is an enrichment of dioxins in the fine particles. This is expected for contaminants that adhere to the surface of particles, since the surface area to mass ratio increases as particle size decreases. Thus, the results from this study may tend to yield results somewhat higher than other studies in which concentrations were measured only in bulk samples.

3.4 Contribution of Specific Congeners

The congener composition of a soil sample may provide useful information about the source of the material, and helps to reveal which specific congeners are contributing the majority of the TEQ levels. Appendix B provides a series of graphs which summarize the relative contribution of each congener to total concentration and to TEQ, both for the full and quantitative analysis approaches. As shown in **Table 4,** the primary contributors to full TEQ values are as follows:

Main Dioxins/Furans
- 1,2,3,7,8-PeCDD
- 1,2,3,4,6,7,8-HpCDD

Secondary Dioxins/Furans
- 2,3,7,8-TCDD
- 2,3,4,7,8-PeCDF
- 1,2,3,6,7,8-HxCDD

Primary PCBs
- PCB-126

3.5 Quality Assurance Samples

Quality assurance samples analyzed as part of this study indicate that the data are reliable and accurate.

Method Blanks

Full TEQ values for 15 method blanks averaged 0.5 ppt (range = 0.1-1.7 ppt). This indicates that there is no significant source in dioxin or PCB contamination within the laboratory.

Splits and Duplicates

The results for split and duplicate pairs were generally in good agreement as shown in **Figure 4**. Summary statistics are presented below:

Type	N	Average Delta (ppt)	Average Ratio
Duplicates	11	6.0	1.6
Splits	12	0.29	1.4

Blind Performance Evaluation Samples

Analytical results for the soil standards (PE samples) obtained from QATS are summarized below.

Sample	TEQ (ppt) (PCDD/PCDF Only) (Mean ± Stdev)			
	Bulk		Sieved	
	Nominal	Measured	Nominal	Measured
Clean Soil	< 2		--	1.7 ± 0.4 (N=21)
Low Standard	35	48 ± 3 (N=2)	--	64 ± 32 (N=8)
Medium Standard	59	75 ± 2 (N=3)	--	117 ± 5 (N=7)

As seen, measured values for bulk PE samples are somewhat higher than but are still in reasonable accord with the expected (nominal) values. For PE samples that were sieved before analysis, the measured values are about twice as high as the nominal values for the bulk PE samples. As noted above, this indicates that dioxins and furans tend to be more concentrated (on a mass per unit mass basis) in fine particles than in bulk soil, as would be expected for a material that adheres to the surface of particles, since the surface area to mass ratio increases as particle size decreases.

Laboratory Spikes

Analytical recovery of congeners from 15 different laboratory spikes (nominal full TEQ = 252 ppt) was good, as summarized below:

Statistic	Full TEQ (ppt)	Recovery
Mean	245	97%
Stdev	9	3%
Min	229	91%
Max	257	102%

4.0 DISCUSSION

Dependence of Dioxin Levels on Land Use

As seen in Figure 3 and Table 3, full TEQ levels for dioxins and furans in area soils are all generally low. However, there are apparent differences in dioxin levels between several different types of land use. Levels in commercial and industrial areas tend to be somewhat higher than in open space and agricultural areas, suggesting that the sources of dioxins in these types of soil are more likely to be local than large-area non-point sources. As noted above, levels in residential samples are similar to commercial levels, presumably because the samples are not from true private residential lots but from governmental properties at least some of which are or may have been used for commercial-type activities.

The distribution of values in each land category were compared using Kruskal-Wallis one-way analysis of variance (ANOVA) on ranks. The results indicated that differences between land uses were statistically significant ($p < 0.001$). Pair-wise comparisons using the Mann-Whitney Rank Sum Test were performed to isolate the groups which were different from each other. The results were as follows:

Statistical Differences ($p < 0.05$)

	Agricultural	Commercial	Industrial	Open Space	Residential
Agricultural					
Commercial	Yes				
Industrial	Yes	No			
Open Space	No	Yes	Yes		
Residential	Yes	No	No	Yes	

As seen, the land use data sets fall into two groups: open space and agricultural lands are not statistically different from each other, but are different from the industrial, commercial and residential data sets. Conversely, the industrial, commercial and residential data sets are not different from each other, but are different from the open space and agricultural data sets. Combining the data into two groups (Open Space/Agricultural, and Commercial/Industrial/Residential) yields the following summary statistics:

Statistic	Agricultural and Open Space	Commercial, Industrial and Residential
N	63	97
Mean	1.7	8.0
Stdev	2.1	13.6
5th	0.2	0.5
25th	0.5	1.4
50th	0.9	3.0
75th	1.5	7.6
95th	6.9	31.6

Dependence on Soil Type

As noted above, soil samples were collected at each sampling station without regard to the soil type at that location. One attribute of the soil type that might be an important influence on dioxin levels is total organic carbon (TOC) since dioxins strongly adsorb to organic material. TOC levels in each sample are being measured, but the results are not yet available.

Comparison to Human-Health Based Guidelines

Although the basic purpose of this study was to characterize the distribution of dioxin samples in soils from the Denver front range area (and not to perform a health risk evaluation), it may nevertheless be of some use to provide a health-based frame of reference by which the distributions may be placed in context. To this end, the USEPA has established default soil screening concentration levels for dioxins that are of potential concern to residents (USEPA 1998a) and workers (EBASCO 1994), as follows:

Residents	1,000 ppt TEQ
Workers	5,000 - 20,000 ppt TEQ

As seen in Table 3 and illustrated graphically in **Figure 5**, none of the samples collected from the greater Denver front range study area approach or exceed the level of concern for either residents or workers.

5.0 SUMMARY AND CONCLUSIONS

The results of this study provide a reliable set of dioxin measurements in a variety of soil sampling locations in and about the Denver front range area. The mean value for full TEQ for dioxins and furans across all samples was about 5-6 ppt, with individual values ranging from less than 1 ppt TEQ up to a maximum of 87 ppt TEQ[1]. Values from open space and agricultural areas tended to be the lowest, while values from industrial, commercial, and residential areas included some higher values. None of the samples collected approached or exceeded the level of health concern for either residents or workers.

[1] Two samples were collected which had TEQ values of 142 and 155 ppt, but these were judged to be outliers that were not representative of typical ambient levels due to non-point sources.

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Table 1. List of Analytes and TEFs

Class	Target Analyte	TEF		
		Mammals	Birds	Fish
Dibenzo-p-dioxins (PCDDs)	2,3,7,8-TCDD	1	1	1
	1,2,3,7,8-PeCDD	1	1	1
	1,2,3,4,7,8-HxCDD	0.1	0.05	0.5
	1,2,3,6,7,8-HxCDD	0.1	0.01	0.01
	1,2,3,7,8,9-HxCDD	0.1	0.1	0.01
	1,2,3,4,6,7,8-HpCDD	0.01	< 0.001	0.001
	OCDD	0.0001	0.0001	<0.0001
Dibenzofurans (PCDFs)	2,3,7,8-TCDF	0.1	1	0.05
	1,2,3,7,8-PeCDF	0.05	0.1	0.05
	2,3,4,7,8-PeCDF	0.5	1	0.5
	1,2,3,4,7,8-HxCDF	0.1	0.1	0.1
	1,2,3,6,7,8-HxCDF	0.1	0.1	0.1
	1,2,3,7,8,9-HxCDF	0.1	0.1	0.1
	2,3,4,6,7,8-HxCDF	0.1	0.1	0.1
	1,2,3,4,6,7,8-HpCDF	0.01	0.01	0.01
	1,2,3,4,7,8,9-HpCDF	0.01	0.01	0.01
	OCDF	0.0001	0.0001	<0.0001
PCBs	3,3',4,4'-TCB (77)	0.0001	0.1	0.0005
	3,4,4',5-TCB (81)	0.0001	0.05	0.0001
	3,3',4,4'-5-PeCB (126)	0.1	0.1	0.005
	3,3',4,4',5,5'-HxCB (169)	0.01	0.001	0.00005
	2,3,3',4,4'-PeCB (105)	0.0001	0.0001	< 0.000005
	2,3,4,4',5-PeCB (114)	0.0005	0.0001	< 0.000005
	2,3',4,4',5-PeCB (118)	0.0001	0.00001	< 0.000005
	2',3,4,4',5-PeCB (123)	0.0001	0.00001	< 0.000005
	2,3,3',4,4',5-HxB (156)	0.0005	0.0001	< 0.000005
	2,3,3',4,4',5'-HxCB (157)	0.0005	0.0001	< 0.000005
	2,3',4,4',5,5'-HxCB (167)	0.00001	0.00001	< 0.000005
	2,3,3',4,4',5,5'-HpCB (189)	0.0001	0.00001	< 0.000005

TEF = Toxicity Equivalency Factor
TEF values are consensus estimates recommended by WHO (Van den Berg et al. 1998)

Table 2. Definition, Application, and Uses of Data Flags

Validation Flags	Meaning of Flags for Dioxin Analyses in Soils and Tissues by the MRI Lab	* **Usability** of **DataSets**	
		Full data set used (*semi-quantitative*)	**Quantitative** (qualified sub-set used)
E	Estimated Maximum Potential Concentration; the relative ion abundance ratios did not meet the acceptance limits.	use value	use ½ value
D	EMPC is caused by polychlorinated **D**iphenyl ether interference.	use ½ value	don't use
B	Analyte was detected in associated Method **B**lank, sample concentration <5x MB concentration.	use value	use ½ value
C	Concentration is above upper **C**alibration Standard; result is an estimate, flagged C by lab and J added by validator.	use value	use value
I	Recovery of 13C-labeled **I**sotopic analyte outside of criteria	use value	use value
J	Estimated: e.g., isotopic standard is outside CCAL range, native analyte recovery in LCS is outside criteria, etc.	use value	use ½ value
NJ	Presumptive evidence for the presence of an analyte with an estimated value; if used for 2378-TCDF, see "U" below.	use ½ value	don't use
S	Peak is **S**aturated; result, if calculated, is flagged by the validator as an estimate - "J".	use value	use value
U	Unconfirmed: column is not specific for 2,3,7,8-TCDF; confirmation not requested. Validator now uses "NJ" flag.	use value	use ½ value
R	Rejected: result is invalid and not usable.	use ½ EDL	don't use
***use of MRI Laboratory's reported "LT" (less than) values* <MQL (10 x Signal:Noise)**			
LT *applied* ***first*** *to data, then apply flags!*	"LT" is not a true "flag", but if a LT result is a "**detect**" **above the MDL** (2.5 x Signal:Noise = lab EDL), then	use value	use ½ value
	"LT" is not a true "flag", but if a LT result is a "**non-detect**" **below the MDL** (2.5 x Signal:Noise = lab EDL), then	use ½ EDL	don't use

* Per concepts in the 1992 EPA Data Usability for Risk Assessment in Superfund guidance, the above flags are to be used for producing two data-sets: 1) a "**Full**" set of semi-quantitative results with an **actual or proxy value for each of the 29 measured congeners**; and 2) a "**Quantitative**" partial set of results with more certain identification and more accurate quantities of congeners which have **no disqualifying flags (D, JN, R or LT) or use limited proxies (E, B, J or U)**. This distinction is made to better understand and limit the artifactual impacts of the less certain estimated values on TEQs, analyzing this sensitivity by comparing TEQs from these two data-sets and evaluating congener profiles with only the analytes that are able to be quantitated.

Source: EPA R8 Soil and RMA Tissue Studies of Dioxins, 2000, ref. RMA/EAL SOP 803

Table 3. Summary Statistics for Full TEQ Levels in Surface Soil Samples in the Denver Front Range Area [a]

Panel A: All Data[a]

Land Use	Statistic				
	N	Mean	Stdev	Min	Max
Agricultural	27	1.6	1.8	0.1	7.7
Commercial	30	11.0	27.2	0.4	141.9
Industrial	30	10.7	18.3	0.2	86.7
Open Space	36	1.7	2.3	0.1	9.6
Residential	39	10.9	25.8	0.2	155.2
Total	162	7.3	19.3	0.1	155.2

a Values above are only for samples for which there was sufficient mass to prepare and analyze the fine fraction. Results for 3 samples which only the bulk samples was analyzed are as follows:

Open space	N = 1	2.5
Industrial	N = 1	3.7
Residential	N = 1	5.6

Panel B: Two Outliers Excluded

Land Use	Statistic				
	N	Mean	Stdev	Min	Max
Agricultural	27	1.6	1.8	0.1	7.7
Commercial [b]	29	6.6	11.5	0.4	57.9
Industrial	30	10.7	18.3	0.2	86.7
Open Space	36	1.7	2.3	0.1	9.6
Residential [b]	38	7.1	10.3	0.2	42.9
Total	160	5.5	11.1	0.1	86.7

b Statistics exclude one data point from the commercial data set and one data point from the residential data set that are judged to be outliers

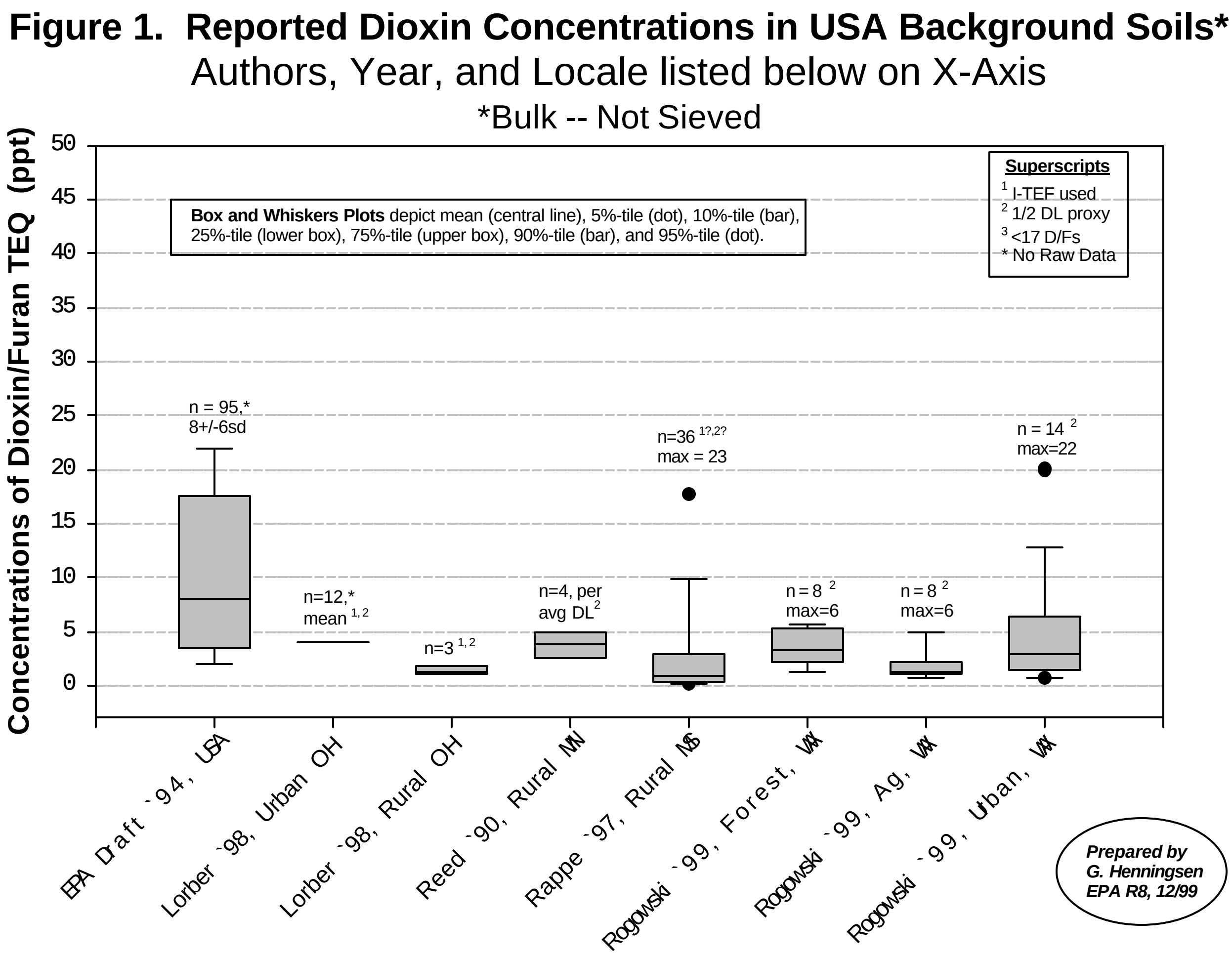
All values are expressed in units of TCDD-Equivalents (TEQ), based on the results for 17 PCDDs and PCDFs (see Table 1). The TEQ was calculated based on the mammalian TEF values shown in Table 1 along with the full concentrations of each congener.

Table 4. Relative Contribution of Congeners to Full TEQ

Analyte	Mean Contribution to Full TEQ					
	Agricultural	Commercial	Industrial	Open Space	Residential	All
2,3,7,8-TCDF	1.2%	0.8%	0.7%	1.7%	0.8%	1.1%
2,3,7,8-TCDD	4.3%	9.6%	3.6%	4.2%	6.8%	5.7%
1,2,3,7,8-PeCDF	0.6%	0.6%	0.4%	0.6%	0.6%	0.6%
2,3,4,7,8-PeCDF	12.4%	7.8%	8.6%	9.1%	8.3%	9.1%
1,2,3,7,8-PeCDD	19.6%	19.0%	16.0%	20.5%	18.0%	18.6%
1,2,3,4,7,8-HxCDF	2.7%	2.2%	2.1%	2.1%	2.1%	2.2%
1,2,3,6,7,8-HxCDF	3.3%	2.5%	2.4%	3.1%	1.9%	2.6%
2,3,4,6,7,8-HxCDF	3.8%	2.7%	2.8%	3.0%	3.0%	3.0%
1,2,3,7,8,9-HxCDF	4.7%	1.9%	1.8%	4.6%	2.0%	3.0%
1,2,3,4,7,8-HxCDD	3.2%	2.8%	3.0%	3.3%	2.9%	3.0%
1,2,3,6,7,8-HxCDD	5.1%	5.8%	5.4%	4.8%	6.2%	5.5%
1,2,3,7,8,9-HxCDD	3.7%	3.8%	3.9%	3.6%	3.9%	3.8%
1,2,3,4,6,7,8-HpCDF	2.2%	2.7%	2.6%	1.5%	2.9%	2.4%
1,2,3,4,7,8,9-HpCDF	0.3%	0.6%	0.2%	0.2%	0.3%	0.3%
1,2,3,4,6,7,8-HpCDD	12.1%	15.6%	15.7%	11.4%	16.6%	14.3%
OCDF	0.1%	0.1%	0.1%	0.1%	0.1%	0.1%
OCDD	0.9%	1.1%	2.4%	0.8%	1.2%	1.3%
PCB-81	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
PCB-77	0.1%	0.1%	0.1%	0.1%	0.1%	0.1%
PCB-123	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
PCB-118	1.0%	1.3%	1.4%	1.3%	1.4%	1.3%
PCB-114	0.1%	0.2%	0.1%	0.2%	0.1%	0.1%
PCB-105	0.5%	0.6%	0.7%	0.7%	0.7%	0.6%
PCB-126	16.8%	16.4%	23.4%	21.4%	18.2%	19.3%
PCB-167	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
PCB-156	0.9%	1.3%	1.5%	1.2%	1.3%	1.3%
PCB-157	0.2%	0.3%	0.4%	0.3%	0.4%	0.3%
PCB-169	0.3%	0.2%	0.2%	0.4%	0.2%	0.3%
PCB-189	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
Dioxins/Furans	80.0%	79.5%	72.0%	74.3%	77.4%	76.5%
PCBs	20.0%	20.5%	28.0%	25.7%	22.6%	23.5%
All	100.0%	100.0%	100.0%	100.0%	100.0%	100.0%

Congeners which contribute 5% or more to the average total TEQ have been shaded

Figure 1. Reported Dioxin Concentrations in USA Background Soils



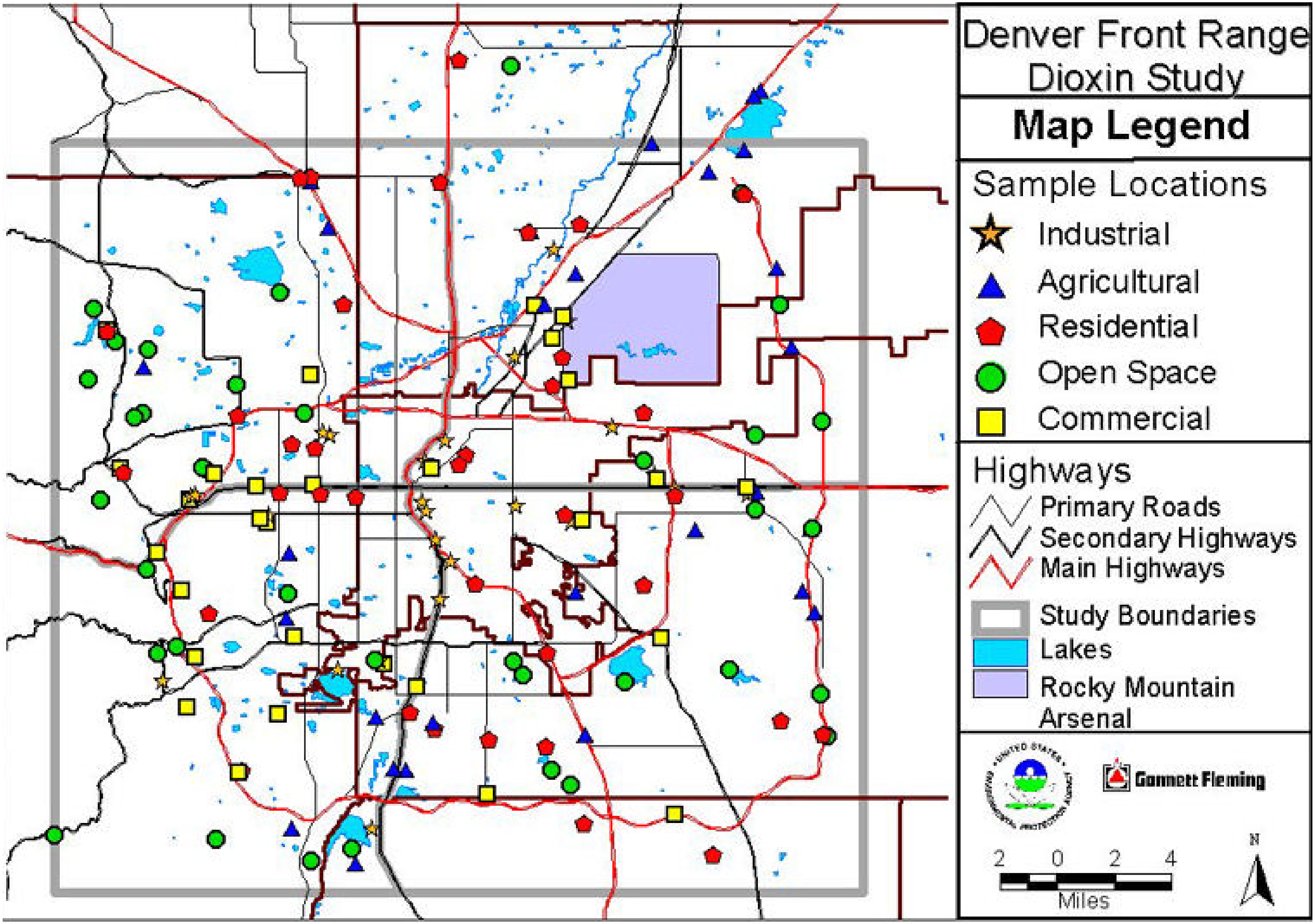
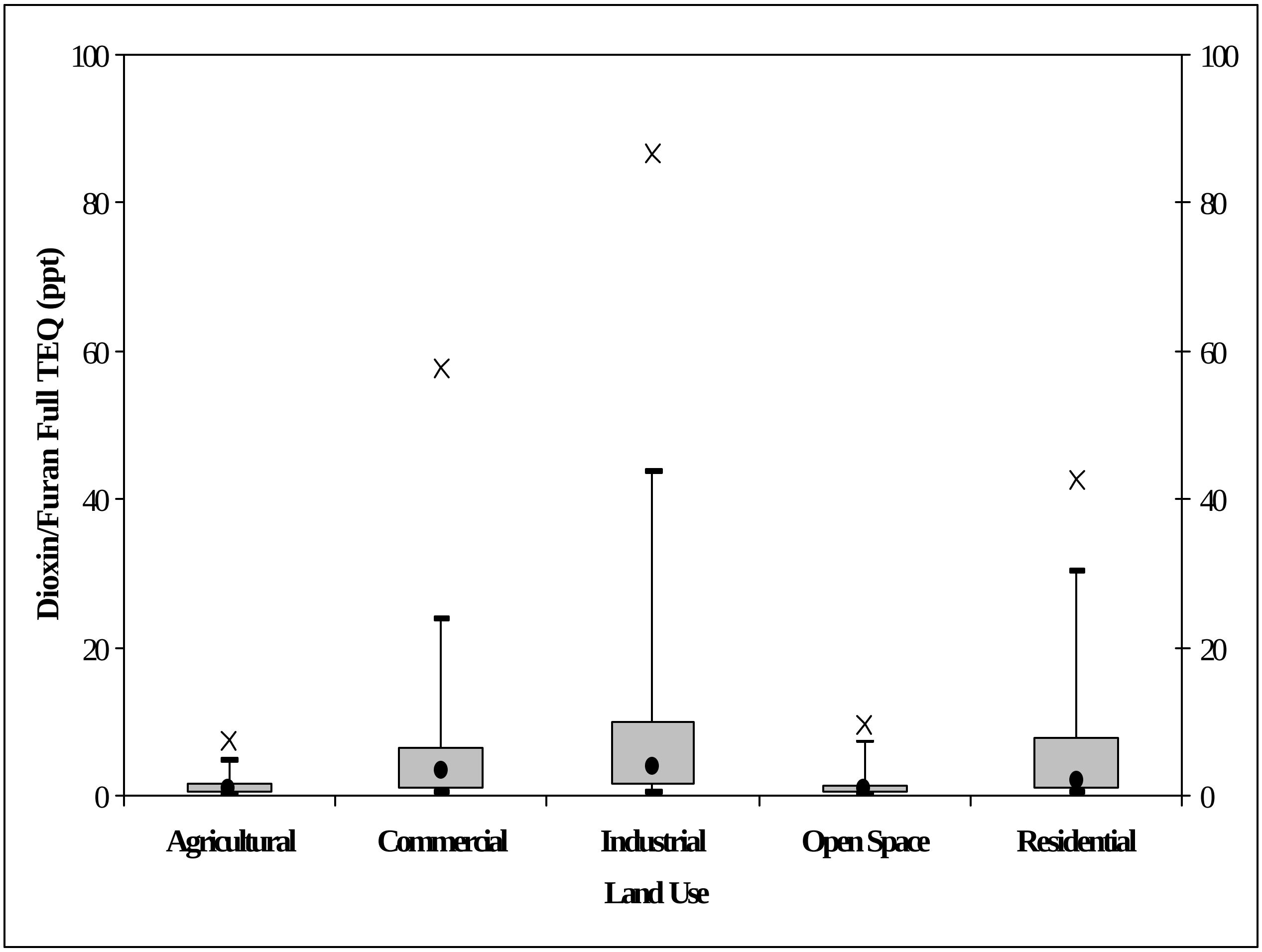

Denver Front Range
Dioxin Study
Map Legend
Sample Locations
Industrial
Agricultural
Residential
Open Space
Commercial
Highways
Primary Roads
Secondary Highways
Main Highways
Study Boundaries
Lakes
Rocky Mountain
Arsenal
Gannett Fleming
2 0 2 4
Miles
N

Figure 3. Distribution of Dioxin Levels (Full) in Denver Front Range Soils



TEQ values are based on 17 dioxin and furan congeners (not including PCBs), and are calculated using ½ the detection limit for congeners that were reported to be below the detection limit.

Figure 4. Comparison of Duplicate and Split Results

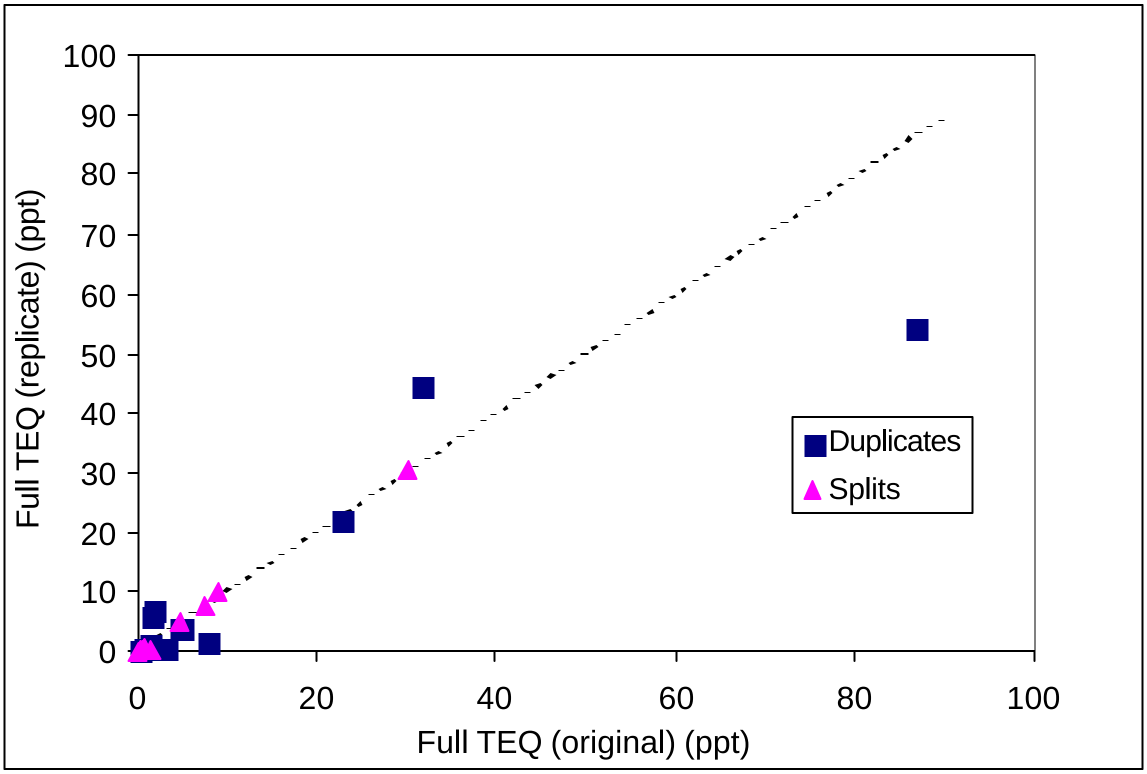


Figure 5. Soil Levels Compared to Health Criteria